



REVIEW

Effect of hybridization on the value-added activated carbon materials

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Received: 30 June 2015 / Accepted: 8 June 2016 / Published online: 16 June 2016
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Abstract This paper provides a concise review of recent advances in activated carbon (AC) and its corresponding modified material. Topics covered in this work include the synthesis and characterization of AC as the feedstock materials, as well as the properties and applications of the subsequent hybrid material for different industries. Numerous research studies have since reported remarkable physical, chemical, thermal, conductivity, porosity, and mechanical (stiffness and strength) properties of AC in different types of multiple material matrices, including polymers, metals, and ceramics. The incorporation of AC particles into material matrices may result in the formation of an entire new class of advanced materials, due to the resulting strong interfacial bonds of the hybrid components. Although this requirement is no different from those that offer conventional hybrid materials, the scale of the reinforcement and filled phase of the AC has changed from micrometers to nanometers. This create opportunities to increase the potential applications of AC hybrid materials of the development of fundamentally unique new materials for in chemical conversion, environmental, and fuel storage applications.

Keywords Nanotechnology · Biomass · Hybrid · Interfacial · Green

Introduction: carbon-based materials

Both nanomaterials and carbon materials are attracting quite a bit of attention within the scope of material science and technology [1–4]. Carbon materials at the nanoscale level, named nanocarbon materials, not only exhibit better properties compared to those of conventional or microscale materials, but also possess new characteristics that conventional materials lack [2, 3]. Recent studies show proved that nanocarbon materials can be used as medical materials, electronic materials and environmental protection materials, all of which are revolutionary materials of the twenty-first century [5].

Activated carbon: advantages

Activated carbon (AC), which is a nanocarbon possessing a sponge-like structure, is made up of small chemically bonded heteroatoms, chiefly oxygen and hydrogen [6–9]. The manufacture of AC mirrors is similar to that of a highly fractal material; both are uniformly formed, with each magnification having tailored pore widths and with pores having an adjustable width [8]. Generally, there are many physical forms of ACs; some examples include granular AC, powdered AC, AC fibers, and AC cloths (Table 1). In synthesizing AC, nearly any carbon-based materials are applicable as precursors [9]. In practice, this includes nutshells and fruit stones, charcoal, wood, peat, soft coal, lignite, petroleum coke, and bituminous coal, among others [8]. Taking into consideration that these materials are high in carbon content and low in inorganic content and composed of a high proportion of carbon and low amount of inorganic components, it makes them suitable for the synthesis of ACs (Fig. 1).

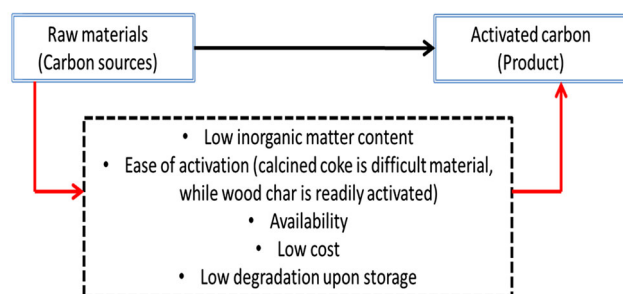
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Table 1 Preparation of different physical forms of AC

| AC categories | Preparation methods | Characteristics | References |
|---------------|---|---|------------|
| Granular AC | Prepared from hard material such as coconut shells and includes particles retained in a 0.177 mm mesh sieve | Column filler for liquid and gas treatments Can be regenerated after utilizing | [10] |
| Powdered AC | Obtained in particles less than 0.1777 mm Usually mixed with the liquid to be treated and disposed afterward | Because of its small particles, the adsorption is normally very effective; however, settling and removal tend to be slower | [11] |
| AC fibers | Prepared from the homogenous polymeric raw material | Indicates a monodispersed pore size distribution Its thin fiber shape enhances intraparticle adsorption and contact efficiencies between the aqueous media | [12] |
| AC cloth | Developed by using a precursor phenolic or viscose rayon | Well thought out to be good adsorbents because of its low pressure drop during the process, flexibility and high contact efficiency | [13] |

**Fig. 1** The selection criteria of raw material for AC production

Furthermore, the heterogeneous surface of AC provides it with extra positive values [9]. The heterogeneous surface property of AC came from two foundations; chemical and geometrical. Geometrical heterogeneity is mainly due to the variation of shape and size of pores, cracks, steps, and pits [10, 11]. Chemical heterogeneity is not only related to different functional groups, chiefly oxygen groups often positioned at the turbostratic crystallites' edges, but also relevant to several surface impurities [12]. Both kinds of heterogeneity result in exceptional absorption properties of ACs. The porous structure of ACs is controlled by the precursor used in the manufacturing process, the activation technique utilized, and the activation amounts [13].

Therefore, AC characterization techniques greatly influence the adsorption rate and capacity. Subsequently, AC was characterized for high carbon proportion, great surface areas, abundant micropores, and narrow or small aperture having the advantage of fast adsorption rate, large adsorption capacity, and simpler regeneration in the gas–liquid adsorption fields [10]. Other leading benefits of AC are its high purity, which prevents poisoning/side reaction, the chemical stability in basic/acidic media, and excellent mechanical performance [12]. Moreover, AC tends to

agglomerate with high specific surface areas and pore volumes, even when lacking microporosity. Pores in the mesoporous range and low tortuosity are formed due to the network-like assembly of AC aggregation, encouraging mass transfer [13]. This is mainly favorable for quick reactions and limited diffusion applications, such as liquid phase uses.

Activated carbon: synthesis and properties

Generally, the AC manufacturing process starts with the carbonization of natural or synthetic precursors at a temperature range of 600–1000 °C, and an activation step at a higher temperature by CO₂ or steam is done afterward [14, 15]. Another method requires chemical activation using alkalis, such as Na₂CO₃, K₂CO₃, NaOH, and KOH, and alkali earth metal salts, such as ZnCl₂ and AlCl₃, and certain acids (H₃PO₄ and H₂SO₄) [16–18]. The aforementioned chemicals are dehydrating agents, which greatly affect the pyrolytic decomposition and inhibit the formation of tar. Thus, the synthesis and characterization of AC reported in many studies indicated that its porosity depends on the activation settings, such as temperature, time, and gas [16].

In chemical activation, KOH and ZnCl₂ significantly affect the precursor's carbonization. ZnCl₂ in particular could be widely utilized as a chemical agent in the AC preparation process [15]. In this process, the carbonization temperature is the most effective factor, followed by heating rate, N₂ flow rate, and residence time [16]. This process causes the aromatization and charring of the carbon skeleton and the formation of porous structures. Firstly, in an inert atmosphere, the raw material was carbonized, while at high temperature, the obtained char was activated using steam or CO₂. In this kind of activation, the raw material was impregnated using an activation reagent and



annealed under inert atmosphere. Several types of natural or synthetic fibers have been utilized since 1970 as AC precursors; examples include polyacrylonitrile, polyphenol, rayon, polyetheretherphthalate, monocarboxycellulose, pitch, and cellulose phosphate [17, 18]. Due to the high cost of synthetic fibers, researchers are trying to benefit from low-cost precursors made from local, cheaper, and readily available material resources. Indeed, AC synthesized from agricultural byproducts has excellent adsorption capacity, significant mechanical strength, and low amounts of ash [19, 20].

Therefore, different ACs have recently been prepared from natural precursors, including jute, coconut fibers, empty fruit bunch (EFB), durian shell, palm kernel shell, almond shell, plum stones, cotton stalks, rice husk, pistachio nut shell, walnut shell, and wood, using chemical and physical activations. The first phase of physical activation involves the thermal treatment of raw fibers at 950 °C under an inert atmosphere, and the second phase contains an activation step with CO₂ at similar temperatures [21]. However, in chemical activation, the raw fiber, usually impregnated in acid solution (H₃PO₄, HNO₃), was annealed at 900 °C. This method leads to the production of numerous acidic surface groups and an interesting porosity of up to 1600 m² g⁻¹ [22–24].

Modification via chemical oxidation/reduction is an effective way of developing the special functions of AC, reduce its usage cost, enlarge the application range, and improve the utilization efficiency [25, 26]. The oxidation of AC introduces CO₂ surface groups, increases the content of O₂-containing acidic groups (such as carboxylic, phenolic, hydroxyl, and ester groups) on the surface of the AC, and enhance the surface polarity/hydrophilicity of AC [27]. Oxidation methods involve using oxidizing gases or solutions. The commonly used oxidants are HNO₃, O₃, KMnO₄, NaClO, H₂O₂, and others [28–30].

Activated carbon: limitation

However, the powder form of AC is plagued with some disadvantages, such as agglomeration and difficulty in filtration due to the fine formation for the slurry phase operation and the high-pressure drop for gas phase operation [18–20]. To overcome these problems, AC is added into large materials or a matrix to form an AC composite system.

Activated carbon: hybrid system

There has been a rapid growth in the use of AC materials as a submaterial in composite systems. Generally, a composite is a material that consists of two or more constituent

materials or phases [31, 32]. The essence of AC composites technology is the capability to correctly place stiff AC at accurate volume fractions and orientations [33].

Activated carbon: polymer hybrid

AC/polymer composites performed well under pressure-driven processes [34, 35]. This combination provides unique mechanical, electrical, adsorption, optical, and thermal properties [36]. Incorporation of AC as fillers modifies the polymer material's characteristics due to the synergistic interaction of polymer-to-AC interfacial bonding [37, 38]. The most noticeable physical effect of AC-based filler is the stiffening (increment on modulus) of the AC/polymer composite system. As AC particle dispersion is mixed at a good polymer-to-AC particle interfacial adhesion, it provides the opportunity to fabricate membranes with enhanced physical properties at low loading necessities [39, 40].

Activated carbon/cellulose triacetate hybrid

One organic polymer that could be incorporated with AC for the fabrication of hybrid membranes via the evaporation method (extensively engaged to achieve plastic films) is cellulose triacetate (CTA) [41–43]. AC/CTA is regarded as a low-priced material possessing superior mechanical, optical, electrical, and thermal properties as opposed to natural CTA [44, 45]. The recorded particle addition of AC alters the composite's characteristics due to the electrostatic interaction between the polymer and the particles' surface, which in turn increases the rigidity of the composites [43]. These properties render it possible for this composite to be used in aqueous phase metal-ion speciation, which serves to exploit the removal behavior of the AC/CTA composites [45].

Activated carbon/polysulfone hybrid

Some studies have focused on investigating the characteristics of AC/polysulfone composites within a continuous operating system. The results proved that the permeability of AC/polysulfone-based membranes is indeed affected by the concentration of AC and particle size. As a result of this, the selectivity of low amounts of carbon with smaller particle sizes was greater [46]. Moreover, the performance of a membrane composed of hybrid AC/polysulfone composites was superior to polymer membranes on its own. One of the important properties of AC particles is their capability to be hydrophobic in natural water, constant electron distributions, and low affinity for polar molecules [47]. The incorporation of AC into polysulfone membrane modifies its chemical properties, porosity, pore size



distribution, and filtration flux. For instance, the high sulfur content of polysulfone on AC improved mercury adsorption, resulting in a three-orders-of magnitude reduction in the concentration of mercury [48, 49]. The X-ray absorption near edge spectroscopic analyses of the mercury bound to AC and to polysulfone on AC seems to suggest that on the surface, the chemical bond with mercury is a combination of Hg–S interactions [47–49].

Activated carbon/polyester hybrid

As the utilization of AC/polyester composites increases in aircraft, ships, and civil industries, it is vital that their corresponding structural performance be determined prior to application, if only for safety reasons [50]. Although some useful information can be obtained from high-temperature oxidation ($>1500\text{ }^{\circ}\text{C}$) and mechanical properties of AC in the context of their potential application in the field of heat-resistant carbon–carbon composites, a small number of studies attempt to understand the mechanism of the oxidation behavior of the composites within a temperature range of most fires, which is normally between 400 and $1100\text{ }^{\circ}\text{C}$ [51, 52]. It was explained that AC was adjacent to the hot surface and exposed to O_2 within the atmosphere, but the surface under AC was exposed to an O_2 -lean environment due to outgassing of volatile compounds released during the decomposition of the polyester matrix impeding the ingress of air into the decomposed material [50]. Thus, AC with and without the presence of O_2 experienced various atmospheric situations, which might influence the final AC/polyester mechanical properties and softening mechanisms [53, 54].

Activated carbon/polysulfide hybrid

As a sulfur-rich polymer material, polysulfide-rubber polymer was incorporated into AC to induce better affinity for the removal of mercury. A long-standing concern with utilizing AC fillers in polysulfide composites is the low softening temperature of the polymer, which could cause weakening, distortion, and failure of heavily loaded composite structures when exposed to moderate temperature fire (above $150\text{--}200\text{ }^{\circ}\text{C}$) [55, 56]. Thus, most research works focused on the structural performance of AC/polysulfide composites under compression loads, where thermal softening of the elastomer matrix is the dominant process controlling mechanical integrity [57].

Activated carbon: metal hybrid

The AC/metal composites possess beneficial and unique physical properties in terms of high void volume, electrical/thermal conductivity, specific surface area, porosity,

and permeability, among others [58]. Compared to the native base metal, the AC/metal composite exhibits high transfer characteristics and effective catalytic/adsorptive properties [59]. The presence of AC facilitates intralayer heating and mass transport of the base metal, allowing for the adsorption and catalytic processes to proceed and sustain it at a meaningfully higher volume, pressures, and temperatures [60].

Many reports have established that the noble metal nanoparticles yield catalysts due to their smaller sizes (1–100 nm) and possess unique electronic, chemical, and physical properties differing from bulk materials, which makes them suitable for constructing novel and enhanced sensing devices, particularly, electrochemical sensors and biosensors [61, 62]. Here, AC is one of the most promising materials considered to be capable for nanoscale construction and the provision of a novel and efficient AC/metal composite [63, 64]. The deposition of noble metals with high dispersion on AC is not a trivial task due to the propensity of noble metals to agglomerate. Another consideration is the interaction of precursor anions and cations with AC, accompanied by the reduction of noble metals [62].

Activated carbon/carbon (C) hybrid

The AC/carbon composites are important as high-temperature lightweight structural materials, such as those used in reentry vehicles, aircraft brakes, and missiles. Since the demand for composite materials has been increasing, the development of methods to fabricate AC/carbon composites with different complex structures is drawing more and more attention [63]. Few studies have reported the fabrication of AC/carbon composites, including reactive metal brazing, solid-state diffusion bonding, a combination of these approaches, and adhesive organic resin bonding, hot pressing, and combustion joining [64, 65]. The monolithic carbon nanotube/AC composite electrodes do not require binder or current collectors, resulting in uniform distribution of the carbon nanotube and high specific surface area of the carbon material (Fig. 2).

However, AC/carbon composites suffer from high fabrication costs due to the need to utilize multiple impregnation–carbonization cycles and techniques, such as chemical vapor infiltration for achieving appropriate densification and acceptable mechanical performances. Additionally, AC/carbon composites also suffer from low ductility, from the brittleness of the matrix of the carbon [66]. To overcome such limitations, recent studies have incorporated ceramic materials, including organoclay, SiC, and carbon black in the AC/carbon composites to improve their density and oxidation resistance at elevated temperatures (Table 2).



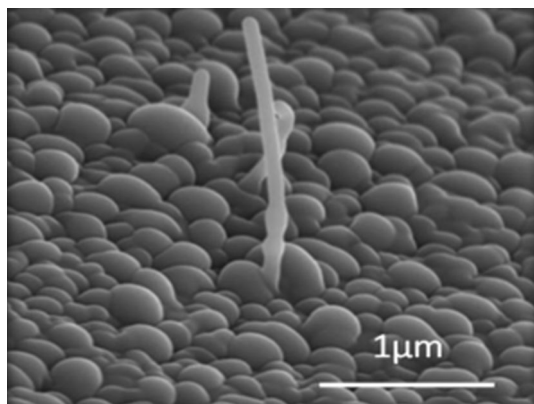


Fig. 2 A straightforward method is presented for the synthesis of carbon nanotube/AC composite electrodes [65]

Generally, the incorporation on a series of fillers to AC/carbon composites with the precursor resin has negligible influence upon the interlaminar shear strength of the resulting composites [69]. Therefore, according to the limited amount of prior work, the effect of growth on the mechanical performances or filler incorporation of AC/carbon composites could be negative or positive [70, 71].

Activated carbon/iron (Fe) hybrid

Some techniques, including reducing, high-energy milling, impregnation, ultrasonic-assisted impregnation, and chemical co-precipitation have been developed to synthesize AC/iron (AC/Fe) composites. However, the AC/Fe composites acquired by these techniques are only capable of retaining a low portion of the porosity of the AC [72]. This is because the pore space of AC is blocked by the presence of Fe particles, which have a low microporous volume and specific surface area [73]. Therefore, some recent studies have impregnated the composites in acid solutions, such as HNO_3 and H_2SO_4 , to the fabrication of Fe precursor, which consequently results in AC composite systems retaining their high porosity [72, 74]. However, this method renders the Fe particles possessing increased particle sizes to be typically deposited on the AC surface. The spent ACs are required to be regenerated before being reused, as after the adsorption of toxic compounds,

especially when dealing with the environmental security application, AC becomes hazardous [73]. This is due to the adsorption only being involved in the transfer of pollutants from wastewater to the AC's surface; however, this does not result in their abolishment.

The most commonly utilized method to regenerate AC/Fe composites is thermal regeneration, microwave regeneration, electrochemical regeneration, advanced oxidation, and extraction with supercritical fluids [75]. From this method, the advanced oxidation process, based on the generation of free OH radical, which degrades most organic pollutants and non-selectivity including $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ or Fe^{3+} and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ or Fe^{3+}/UV radiation, seems to be a promising method as it is simple and easy to run [76, 77].

Activated carbon/gold (Au) hybrid

Generally, the combination of AC and gold nanoparticles results in interesting properties due to the active surface of the AC materials. Several types of O_2 groups found on the AC's surface, which were selectively maximized via chemical and thermal processes, were utilized as building blocks for the covalent attachment of gold nanoparticles [78]. Most approaches for gold decoration of AC include physical evaporation, attachment after oxidation, and solid-state reaction with gold salt at elevated temperatures and electro-less deposition from salt solutions with the aid of reducing catalysts or agents [79]. The amount of carbon, hydrogen, nitrogen, and oxygen functional groups, with a highly porous nature of AC, may greatly inhibit Au nanoparticles on the AC surface [78, 80]. A novel mild method for the preparation of AC/gold composites through the direct reduction of Au^{3+} ions onto the surface of AC has been reported. To acquire a high metal dispersion, gold nanoparticles were deposited on the AC solution of ethylenediamine complex $[\text{Au}(\text{en})_2]\text{Cl}_3$. The phenolic group could attach itself to Au^{3+} ions, resulting in the formation of small gold nanoparticles after the reduction of H_2 [80, 81]. The chemically modified AC was obtained by the gas-phase oxidation of the latter to introduce surface O_2 groups. These groups have properties that relegated the AC as a support material to the gold precursors [78]. The concentration and the nature of different functional groups are known to depend on the AC pretreatment by bases and

Table 2 Mechanical properties of AC/carbon composites with different incorporation materials

| Composites system | Mechanical properties (flexural strength MPA) | Density (g cm^{-3}) | References |
|----------------------------|--|--------------------------------|------------|
| AC/carbon composites + SiC | 82–120 | 1.52–1.57 | [67] |
| AC/carbon + carbon black | 15–42 | 1.52–1.67 | [68] |
| AC/carbon + CNTs | 179–233 | 1.52–1.70 | [69] |



acids, which could be controlled by thermal treatment in different atmospheres.

The AC/gold composites have been found to be catalytically active for a plethora of different reactions, such as redox process, hydrocarbon oxidation under mild conditions, oxidation of CO, hydrochlorination of acetylene, oxidation of hydrocarbons, hydrogenation of CO₂, reduction of nitric oxide, and oxidation of glycerol [82, 83]. As a matter of fact, industrial chemical processing and environmental protection are foreseen as significant future applications of AC/gold composites. Also, it was reported that the AC/gold composites play a crucial role in electrocatalytic reactions and greater electrocatalytic activities for the detection of some small molecules, including hydrazine. Notably, the AC/gold composite exhibits a sharp peak at a much lower oxidation potential (0.13 V) with threefold current and a very low hydrazine detection limit of 6.3 nM [84].

Activated carbon/platinum (Pt) hybrid

Generally, the AC/platinum (AC/Pt) composite is prepared by vacuum treatment and heat reduction. The vacuum treatment helps infuse the precursor of Pt into the pores of AC. The specific surface area and pore structure of the whole AC/Pt composites would change after the impregnation of Pt nanoparticles [85, 86]. The characterization results indicated that the modified vacuum treatment effectively decreased the size and improved the dispersion of Pt nanoparticles [85, 87]. Furthermore, the impregnation condition of Pt nanocrystals obviously influenced the specific surface area and pore structure of the AC/Pt composite. Indeed, by varying the pH value and heating approach, and the size and amounts of loading Pt nanoparticles, its properties could be tuned. It was confirmed that lower pH values and higher reaction temperatures would be conducive to larger Pt nanoparticles when the amount is sufficient [88, 89].

Recently, AC/Pt composites attracted extensive attention due to its low costs, easy obtainment, complete reversibility, lightweight, fast kinetics, and high surface area [90, 91]. From these advantages, Pt-impregnated AC has been widely applied for energy storage. For example, in hydrogen storage application, even with much lower surface area and pore size, tiny Pt nanoparticles were uniformly distributed within the pores, effectively assisting in hydrogen diffusion into the deeper sites of AC via the spillover phenomenon [92, 93]. There were reports of AC/Pt composite as being very active and selective for degradation of low molecular weight carboxylic acid [94].

Activated carbon/silver (Ag) hybrid

The antibacterial and catalysis effects of AC were improved by the incorporation of metallic silver in the AC/

silver composite. This beneficial property originates from silver ions dissolving on the surface of bulk silver [95]. The oxidation of metallic silver to active silver ions proceeds through the interaction of silver with H₂O molecules [96]. This, in turn, results in the high versatility of AC/silver composites, which is often regarded to be due to the presence of multiple Ag–O interactions. Oxygen molecules can be physically and chemically adsorbed on the surface of AC/silver composites, which in general favors deep oxidation reactions in the form of lattice oxygen, located in bulk, and is usually treated as inactive and in intermediate species, which are responsible for the selective oxidation reactions [97, 98]. AC/silver composites release silver ions into the pathogenic environment for it to be effective. This will allow the composites to purify drinking water, which is a potential application for this composite. The catalytic properties of AC/silver composites are also practical for the liquid phase epoxidation of cyclohexene. This process results in the production of cyclohexene oxide [99]. On a practical scale, AC/silver composites require optimization to its surface area, antibacterial activity, and the amount of silver lost. The catalytic activity of AC/silver composites is remarkably sensitive to the crystallite size of silver, the nature of support matrix, surface protecting ligands, synthesis methods, as well as pre-treatment conditions of the AC/silver composites [100].

The traditional methods for preparing AC/silver composites are impregnation and precipitation, which are convenient and usually involve a step of the high temperature of calcination that converts silver precursors into active components [101]. In some cases, high-temperature calcinations could induce the agglomeration of silver nanoparticles on the AC support, particularly for silver particles not interacting or interacting weakly with the AC support, which would eventually affect the final properties of the composites [102]. To date, most of the AC loaded with silver is prepared via impregnation with AgNO₃, which involves soaking AC in a solution of AgNO₃, followed by reduction using agents such as formaldehyde and/or hydrazine, or simply by heating. However, AC/silver composites prepared through this method is associated with uneven distribution of silver onto AC surface [97]. In terms of applications, the silver particle of the composites decreases remarkably as the contact time increases. The sudden and drastic removal of silver particles is mainly due to the low resistance of the AC/silver composites, brought about by the attrition mechanism [98, 103]. This is due to the silver particles' dissociation from the AC surface. As a result, the antibacterial activity of the AC/silver composites will decrease over time. The current attempt to address this problem is to utilize silver ions instead of bulk silver [104]. Indeed, it is difficult to use bulk silver in industrial or domestic applications due to its high costs and low rates of



ion release. Compared to bulk silver, silver ions are long lasting, cheap, and subject to controlled release. Furthermore, AC/silver composites are used in material and optical science, separation technology, and pharmacy [105, 106].

Activated carbon/copper (Cu) hybrid

AC/Cu composites demonstrate a promising activity and selectivity toward diesel distillation while lowering methane selectivity [60]. This combination can be attributed to the specific behavior of AC with high surface area and weak interaction between metallic Cu active sites and AC [107, 108]. It should also be emphasized that the pore size of AC is crucial toward restricting the growth of the carbon chain to the wax [109]. Cu supported on AC demonstrated higher efficiency in the treatment of dyeing and printing wastewater compared to alumina support [110, 111].

Activated carbon: metal oxide hybrid

From carbon molecular sieves, AC/metal oxide composites are made up of inorganic oxides dispersed within the AC matrix. AC/metal oxide composites have been used for a variety of chemical reactions (Table 3). Among the metal oxide catalysts, transition metals occupy a predominant place, owing to their low production cost, easy regeneration, and selective action.

Activated carbon/iron oxide (Fe_3O_4) hybrid

The combination of iron oxide (Fe_3O_4) and AC resulted in composite materials that possess high adsorption capacity and easy recovery via its inherent magnetic properties [112, 113]. The AC/ Fe_3O_4 powder composites were encapsulated within biopolymer beads such as alginate or chitosan to induce magnetic sorbent with high adsorption capacity. Indeed, the presence of Fe_3O_4

did not significantly affect the surface area or the pore structures of the AC [117, 118]. For example, AC/ Fe_3O_4 composites have been explored as highly effective heterogeneous Fenton catalyst for the degradation of organic pollutants due to the significant promotion of H_2O_2 decomposition [119]. Thus, it is anticipated that AC/ Fe_3O_4 composites would have high regeneration efficiency through H_2O_2 . Here, AC/ Fe_3O_4 composites, combining the adsorption features of powdered AC with magnetic and excellent catalytic properties of Fe_3O_4 nanoparticles, are expected to possess a high specific surface area and porosity [120].

The superparamagnetic property of the external magnetic field of the composites can be manipulated [119]. For example, some Fe_3O_4 , such as the amorphous hydrous ferric oxide (FeOOH), poorly crystalline hydrous ferric oxide (ferrihydrite), and goethite $\alpha\text{-FeO}(\text{OH})$ are promising adsorptive materials to remove arsenic from aqueous solutions. These forms of Fe_3O_4 retain their strong affinities to arsenic, but are limited to reactor configurations incorporating large sedimentation and filtration units [120, 121]. Therefore, the comparison between the adsorption isotherms of arsenic (as a model of pollutant compound) from aqueous solution onto the AC/ Fe_3O_4 composites and virgin AC showed that the composites have an excellent capacity for adsorbing arsenic, with 0.01 mg L^{-1} of removal within 1250 mL empty bed volume [122].

There are various methods of preparing AC/ Fe_3O_4 composite being reported in literature. One of these involves utilizing special ferric oxide microcrystal. The main phase making up this composite is magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), and goethite ($\alpha\text{-FeO}(\text{OH})$). Another synthesis method is the surface functionalization process [123–125]. The AC's surface is treated by FeSO_4 solution at various pH, temperatures, and ionic strengths [126]. Meanwhile, another approach involves impregnating FeCl_2 to AC treatment, followed by chemical oxidation [127].

Table 3 AC/metal oxide composites with their respective applications

| AC/metal oxide composites | Application | References |
|---|--|------------|
| AC/ Fe_2O_3 , AC/ ZnO and AC/ TiO_2 | Degradation of organic compounds | [112] |
| AC/ Fe_2O_3 | Hydroxylation of benzene | [113] |
| | Dehydrogenation of propane | |
| | Acylation of alcohols | |
| AC/ WO_3 | Decomposition of methanol and ethanol | [114] |
| | Combustion of toluene | |
| | Hydrogenation of ethylene | |
| | Isomerization of 1-butene | |
| AC/ SnO_2 | Low-temperature oxidation of CO | [115] |
| AC/ Al_2O_3 | Hydroprocessing and hydrodesulfurization process | [116] |



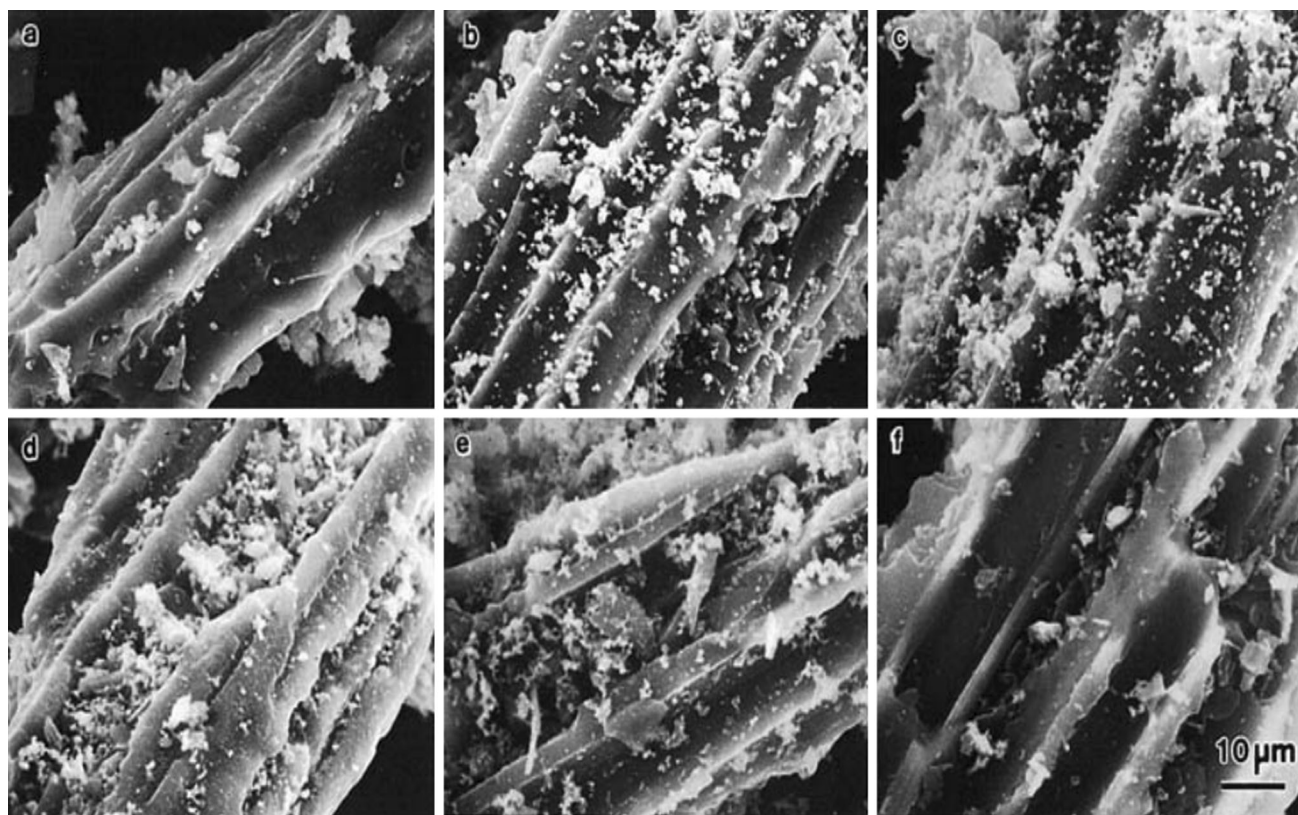


Fig. 3 Scanning electron microscopy (SEM) micrographs of AC/TiO₂ composites prepared at various subcritical and supercritical conditions of iso-propanol for 1 min. **a** 250 °C. **b** 300 °C. **c** 350 °C. **d** 400 °C. **e** 450 °C. **f** Micrograph of AC is included for comparison [129]

Activated carbon/titanium oxide (TiO₂) hybrid

The synergistic increase in the activity of AC/TiO₂ composites have been reported, most of which was attributed to the presence of a common contact interface between the solids, where the AC captures the pollutants by adsorption, allowing them to migrate continuously to the supported photocatalyst due to the presence of concentration gradients [128, 129] (Figs. 3, 4). However, the need for the incorporation of visible light-active photocatalysts into the AC/TiO₂ composites has been emphasized in literature. Additionally, the composites were reported to suffer from biofouling and the formation of biofilms due to the biocompatibility of AC [130, 131].

To address practical issues related to separation of suspended photocatalysts from slurry, the development of magnetically recoverable AC/TiO₂ photocatalyst has become an active field of research [132–134]. Some studies proposed the hybridization of magnetic removal strategies with adsorbent AC/TiO₂ composites by synthesizing AC/TiO₂-magnetic composites, prepared by impregnating mixed-phase Fe₃O₄ into AC, followed by sol–gel synthesis to deposit TiO₂ photocatalyst into composites, culminating in the evaluation of the photocatalytic activity for phenol degradation under UV light [135–137].

Activated carbon/tin oxide (SnO₂) hybrid

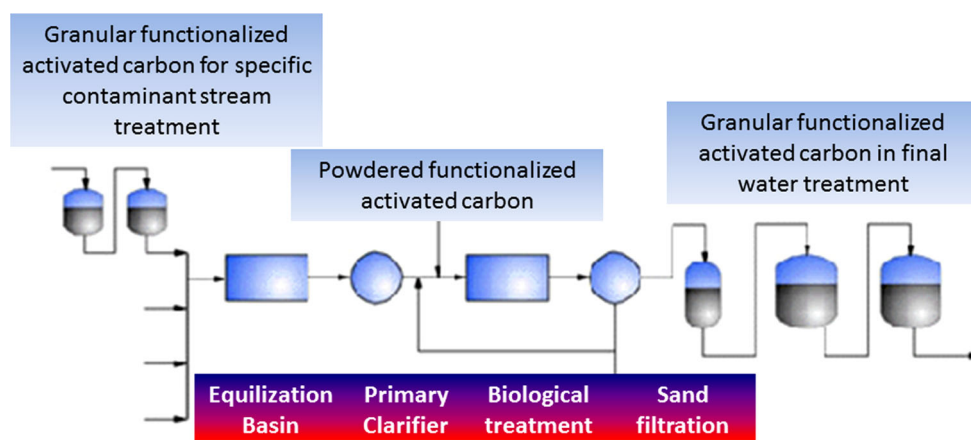
In other studies, the AC/SnO₂ composites were prepared by wet impregnation and oven drying at 120 °C. The subsequent heat treatment on the resulting products was done at 200 or 850 °C in inert atmospheres, with SnCl₂ acting as the metal oxide precursor [138]. The AC/SnO₂ was then texturally characterized by N₂ adsorption at –196 °C, mercury porosimetry, and density measurement. It was found that the macro–meso and microporosity of AC/SnO₂ composites is significantly greater than the parent AC or SnCl [139]. It was also confirmed that by heating it to 850 °C, the pore size distribution of AC/SnO₂ composites becomes uniform within the three porous regions. The textural modifications have been associated with mass, composition, and structural modifications [140].

Activated carbon: ceramic hybrid

AC is classified as an encouraging functionalized element, which provides the ceramic composites multifunctional characteristics due to its outstanding physical properties. Researchers have proven that combining AC into ceramic matrices will result in composites with highly enhanced mechanical and electrical properties. A few studies involved



Fig. 4 The application of granular and particle AC as adsorbent for the water purification process



synthesizing AC/ceramic composites with boosted thermo-physical properties. One of the main difficulties is the large interfacial thermal resistance between AC and ceramic matrices, which radically increases phonon scattering, and accordingly decrease the interfacial thermal transfer within the composites. As a result of this, adapting the interfacial structure of the AC/ceramic composites to reduce the interface thermal resistance is regarded as one of the main concerns.

Activated carbon/alumina (Al_2O_3) hybrid

Alumina/AC composite was synthesized via the catalytic growth of AC on $\gamma\text{-Al}_2\text{O}_3$ wash-coating layer covering the walls of the ceramic monolith. This composite has a moderately uniform mesoporous layer of AC, with a quite small diameter [141, 142]. The thin alumina wash-coating stops the AC from being trapped in the Al_2O_3 pores, and the AC can be easily produced throughout the wash-coating layer to create a uniform layer of AC that entirely covers the surface of monolith growth [143]. The combined AC/alumina has the benefit of being capable of damaging the adsorbed gases or liquids and excellent catalytic behavior, which provides it the opportunity to be effective in applications such as destructive filtration and protecting system [144, 145] (Fig. 4).

Activated carbon/cerium oxide (CeO_2) hybrid

To increase the catalytic activity of CeO_2 , it has to be dispersed onto the AC's surface. This will increase the available surface area of the CeO_2 and electron transfer between CeO_2 and AC. The catalytic activity of AC/ CeO_2 composites was studied for ozonation of oxalic acid and aniline, and it was found that the AC/ CeO_2 composites were excellent for this intended application [146]. Several studies exploited novel AC/ CeO_2 composites with enhanced photocatalytic activity. For example, the adsorption and photocatalytic properties of AC/ CeO_2

composites were determined by adsorbing and degrading 4-chlorophenol in aqueous solution [147]. The results showed that the adsorption and photocatalytic activity were significantly enhanced compared to pure CeO_2 .

The efficiency of the composites is mainly affected by the amount of Ce^{3+} species on the surface. The use of AC as a support structure also favors the removal of both organic compounds [148, 149]. Recent studies have focused on the catalytic activity of CeO_2 in ozonation reactions and investigated a possible synergistic effect between AC and CeO_2 in the ozonation of organic compounds [150]. AC itself has been proved to be an efficient ozonation catalyst [150, 151]. Some novel synthesis techniques for highly dispersed CeO_2 nanoparticles on AC have been developed, namely, the AC/ CeO_2 composite was prepared by the impregnation method, with cerium nitrate salt, boiling reflux of ethylene glycol, and simple solvothermal method [150].

Activated carbon/clay hybrid

AC/clay composites were prepared in monolithic forms with different wall thicknesses and channel widths, and as solid and tubular extrudates [152–154]. The adsorption capacity of AC/clay was studied in terms of vapor pressure of the gas to adsorb and the pore size distribution of the resulting composites. Using toluene as a contaminant, it was confirmed that the adsorption capacity of AC/clay composites offers a sufficiently large and easily accessible external surface area [155, 156]. The initial adsorption takes place at slower diffusion into the narrow microspores of AC/clay composites, where the contaminant is more strongly adsorbed.

AC hybrid: applications

AC composites are applied to a variety of areas, such as adsorbents in air, water, and pollution control, and catalytic supports in the chemical and petrochemical industries.



Chemical conversion application

One of the more common applications of AC is as catalyst support in an AC composite system. ACs are suitable for this as its physical, chemical, and surface nature can be tailored for the intended applications [85]. It can be surmised that the textural properties of AC not only have a significant influence upon catalyst dispersion, but also affect the reduction of metal chemical species, especially in the case of the conventional incipient wetness impregnation technique in the production of AC composites. The surface functional groups, especially O_2 complexes, on the AC, not only offer anchor sites for the catalyst precursor, but also play an important role as active centers in a multifunctional catalyst due to their acid–base or redox properties [88, 89]. Another advantage of the surface groups is that they increase the access of metal solutions from the reduction of the hydrophobicity of the AC. When the AC acts as a microporous material, it is texturally susceptible to the support of the catalysts on its surface. In most cases of AC/metal oxide composites, the AC acts as a metal oxide support, which may be employed as an active catalyst simultaneously [100, 129]. The hybrid AC/metal oxide catalyst is suitable for utilization within similar catalysis reaction as AC and metal oxide on its own [88]. There are two routes to determine the catalytic activity of the AC/metal oxide composite catalyst: specific activities of AC and metal oxide, and their respective contents within the samples [133].

Environmental applications

For environmental application such as petroleum refining, wastewater treatment, air pollution treatment, and volatile organic compound adsorption, one of the major technologies for the removal of various organic compounds is adsorption by AC (Table 4) [94, 97, 98]. However, the applications are limited by difficulties encountered during the separation and regeneration processes. After becoming exhausted, the adsorbed AC composites need to be separated from the aquatic system and regenerated (Fig. 5).

Table 4 AC hybrid in environmental applications

| AC hybrid system | Environmental applications | References |
|-------------------------------------|---|------------|
| AC/TiO ₂ | Adsorbent of organic substances of propionaldehyde, propylamide and bromoform | [32] |
| AC/nitric acid and thionyl chloride | Mercury removal | [29] |
| AC/polystyrene | Emulsion oily waste treatment | [35, 36] |
| AC/bagasse | Phenol removal and treatment | [44] |
| AC/TiO ₂ | Leachate treatment | [33] |

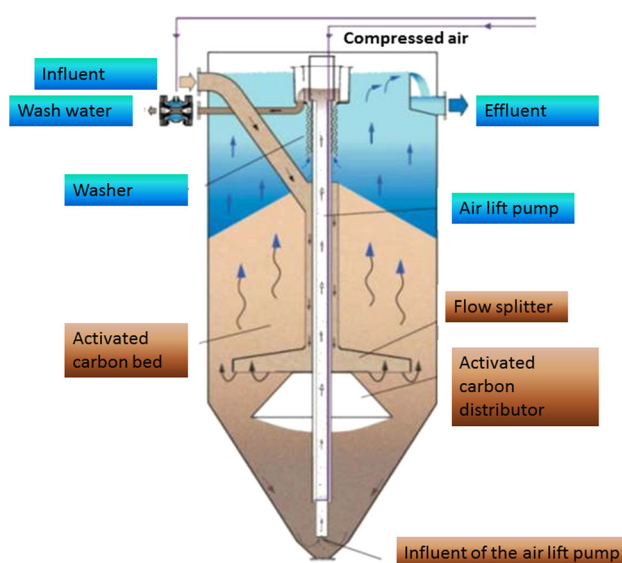


Fig. 5 The application of functionalized AC on water treatment

However, the separation normally involves complex procedures such as filtration or centrifugation [145].

For example, the adsorption experiment by AC/Fe₃O₄ composites showed that the methyl orange (model of dye compounds) sorption process followed the pseudo-second-order kinetic model and the adsorption isotherm data could be simulated using the Freundlich model [155–154].

Fuel

Securing our energy future is the most important problem that humanity faces in this century. Burning fossil fuels is not sustainable, and a wide use of renewable energy sources will require a drastically increased ability to store electrical energy. In the move toward electrical economy, chemical (batteries) and capacitive energy storage (electrochemical capacitors or supercapacitors) devices are expected to play an important role. This account summarizes research in the field of electrochemical capacitors conducted by hybrid AC materials.

Overall, the combination of the AC as electrode materials with a proper electrolyte can successfully increase both the energy stored by the device and its power, but no perfect active material exists and no electrolyte suits every material and every performance goal. AC with high surface areas and porosities that range from subnanometer to just a few nanometers matched with the electrolyte ion size can provide high energy density. Thus, it can provide high power due to fast ion sorption/desorption on their outer surfaces (Figs. 6, 7). AC hybrids are most widely used on the industrial scale as an adsorbent for the electrode materials in electrochemical devices and processes, due to their high specific surface area, adequate pore size



Fig. 6 AC hybrid adsorbent via multicomponent adsorption of CO_2 , N_2 , and H_2O [157]

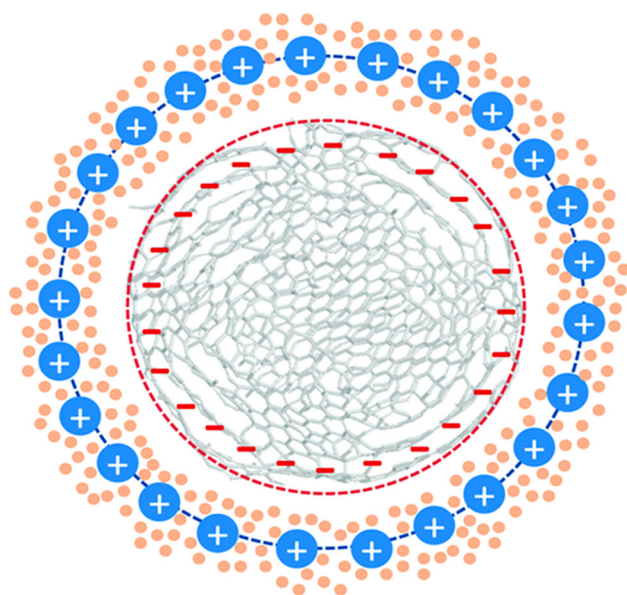
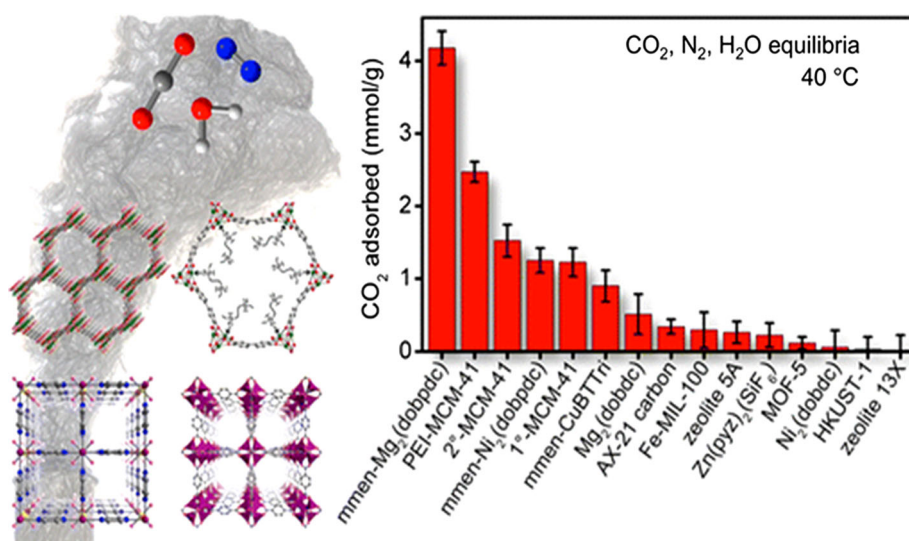


Fig. 7 Capacitive energy storage in nanostructured AC hybrid material [158]

distribution, variable characteristics of surface chemistry, and relatively high mechanical strength [26, 33, 37, 68] (Table 5).

Conclusion

AC hybrid has been receiving more and more attention recently due to their unique properties such as low density, high specific surface area, and thermal stability. Increased applications of these composites, especially in the industry, require the development of suitable synthesis routes and analytical methods for the purpose of quality control. Activated carbon fillers, with excellent mechanical, conductivity, and thermal performance to weight ratio, are preferred for advanced composite applications. The focus is primarily on the high technology sector, which includes chemical conversion, environmental, fuel, or other areas, where the large-scale use of AC is driven by maximum performance instead of cost. However, a significant degree

Table 5 AC hybrid in energy applications

| AC hybrid system | Energy applications | References |
|-----------------------------------|---|------------|
| AC/MnO ₂ | Electrochemical hybrid capacitor with energy density of 28.8 Wh/kg at current density of 0.25 A/g | [62] |
| AC/poly(3-methylthiophene) | Long-term viability of this ionic liquid as green electrolyte for high-voltage hybrid supercapacitors | [38] |
| AC/poly(3-methylthiophene) | 3 V and 1.5 kF preseries supercapacitor modules and 2 kW stacks | [40] |
| AC/NiO ₂ | The maximum of the specific capacitance and energy density of the hybrid supercapacitor were 73.4 F/g and 26.1 Wh/kg at the current density of 0.1 A/g and operating temperature of 40 °C | [58] |
| AC/TiO ₂ /GO | At a voltage range from 1.0 to 3.0 V, 42 W h kg ⁻¹ of energy is achieved at 800 W kg ⁻¹ | [51] |
| AC/Fe ₃ O ₄ | Good cycling performance; it remains approximately 96 % of initial capacity after 800 cycles at a charge/discharge rate of 4 C | [75] |



of discrepancy still exists, especially with regard to the mechanical and conductive properties of AC composites. There is need for a different and more comprehensive approach for the development of activated carbon composites used in commercial high technology sector. Therefore, integrated efforts are being made in these and other possible directions to reduce the existing gap between theoretical and practical tensile strengths and improved compressive behavior of AC composites.

Acknowledgments This work was financially supported by the University Malaya Research Grant (UMRG RP022-2012E) and Fundamental Research Grant Scheme (FRGS: FP049-2013B) by Universiti Malaya and Ministry of High Education, Malaysia, respectively.

Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this paper.

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